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Optical and luminescent properties of ceria nanoparticles produced by gas phase method

Myshkina A V^{1,*}, Bazhukova I N¹, Kiryakov A N¹, Sokovnin S Y^{1,2}, Il'ves V G², Kasyanova V V¹

¹ Ural Federal University, 19 Mira St., Yekaterinburg, Russian Federation

² Institute of Electrophysics, UB RAS, 106 Amundsen St., Yekaterinburg, Russian Federation

*a.v.myshkina@urfu.ru

Abstract. The study on luminescent and optical properties of ceria nanoparticles allow one to indirectly assess the defectiveness of the material crystal lattice. The decomposition of the luminescence spectrum in the Gaussian bands shows the presence of Ce^{3+} ions in the CeO_2 crystal lattice, as well as optical active centers, probably associated with oxygen vacancies. These characteristics permit us to estimate the relative amount of Ce^{3+} ions in the crystal lattice and could be considered as an important prerequisite for the use of nanoparticles as redox agents in industry and medicine.

1. Introduction

Cerium dioxide nanoparticles are a promising material for use in industry, chemistry, medicine and biology [1,2]. Interest in the use of this material is due to the unique properties that appear in the transition state in the nanoscale. Nanocrystalline cerium dioxide is characterized by an increase in the lattice parameter and, as a consequence, the formation of structural defects. [3]. Such defects include defects associated with oxygen vacancies (F , F^+ and F^{++} centers), as well as Ce^{3+} centers, resulting from Ce^{4+} ions reduction near to oxygen vacancies [4]. These defect centers expressed cause the oxygen nonstoichiometry ceria nanoparticles and, consequently, the activity of the material participation in redox reactions. The recent studies have shown the key role of such defects on redox properties of material. The CeO_2 nanoparticles appear antioxidant properties in case of the Ce^{3+} ions presence [5]. On the contrary, highly stoichiometric nanoparticles with the prevalence of Ce^{4+} ions behave like oxidases and lead to reactive oxygen species (ROS) generation [6]. Therefore, the ratio of ($\text{Ce}^{3+}/\text{Ce}^{4+}$) is a crucial factor determining activity of CeO_2 nanoparticles.

Also Ce^{3+} ions and defects associated with oxygen vacancies are capable of forming luminescent active centers. The luminescence spectra of nonstoichiometric ceria possess $5d \rightarrow 4f$ luminescence of ions Ce^{3+} , F^0 -center luminescence, and the luminescence from the charge transfer complex $\text{Ce}^{4+}-\text{O}^{2-}$. [7]

The study of the optical and luminescent properties of cerium dioxide nanoparticles allows us to draw conclusions about the nature of these emission bands, as well as provides information on the electronic structure of nanoparticles. This data could be use for material modification with the purpose of properties enhancement.

Recent studies have investigated the optical and luminescent properties of nanoparticles obtained by chemical methods, such as sol-gel method, coprecipitation, hydrothermal. The study of the



luminescent properties is characterized by intense absorption in the UV region and weak luminescence in the region of 2.5 -3.5 eV [8] At the same time the nanoparticles obtained by physical methods, such as electron beam evaporation method, less studied in detail.

The purpose of this work is to study the optical and luminescent properties of cerium dioxide nanoparticles synthesized by the gas-phase method of electron beam evaporation of ceramic targets.

2. Materials and methods

CeO₂ nanoparticles was obtained by a pulsed electron beam evaporation in a low pressure gas on a NANOBIM-2 installation. [9]. The details of nanomaterial synthesis correspond to papers [10].

The nanoparticles powder was pressing at a pressure of 10 MPa. The tablets diameter and thickness was 6 mm and 1 mm respectively. The suspensions of ceria nanoparticles were stabilized by sodium citrate and sounded for 40 minute by ultrasound (PSB-Gals). Suspension concentration was 500 µg/ml.

Diffuse reflection spectra of ceria nanoparticles tablets were registered by Lambda 35 spectrophotometer using RSA-PE-20 integrating sphere within 190 to 1100 nm range at 120 nm/min scanning speed. Calculation of band gap was performed using Kubelka-Munk function and Tauc method. [11]

The photoluminescence spectra of ceria nanoparticles suspension were recorded by FL3C-2iHR320 (HORIBA Instruments Inc) equipped with xenon lamp.

3. Results and discussion

3.1. Characteristics of nanoparticles

Nanoparticles of cerium dioxide obtained by electron beam evaporation have a grain size of 3-5 nm and a specific surface area of up to 190 m²/g [10]. The strong non-equilibrium conditions of this synthesis method could lead to higher oxygen non-stoichiometry of cerium oxide and, consequently, to a high amount of oxygen vacancies and Ce³⁺ ions. These data may be a prerequisite for the high defectiveness of nanoparticles and their high catalytic activity.

3.2. Diffuse reflectance spectroscopy

The figure 1 shows the diffuse reflectance spectrum by ceria nanoparticles tablets. The spectrum was transferred to the Kubelka-Munk model (1), and then the band gap was calculated by Tauc method (2).

$$F(R) = \frac{(1-R)^2}{2R}, \quad (1)$$

where R – reflectance index, %.

$$f(F(R) \cdot h\nu) = (h\nu - E_g)^n, \quad (2)$$

where n=2 and ½ for direct and indirect band gap respectively.

The obtained band gaps of 3.18 eV for direct transitions and 2.48 eV for indirect transitions correspond to the standard values for cerium oxide [12]

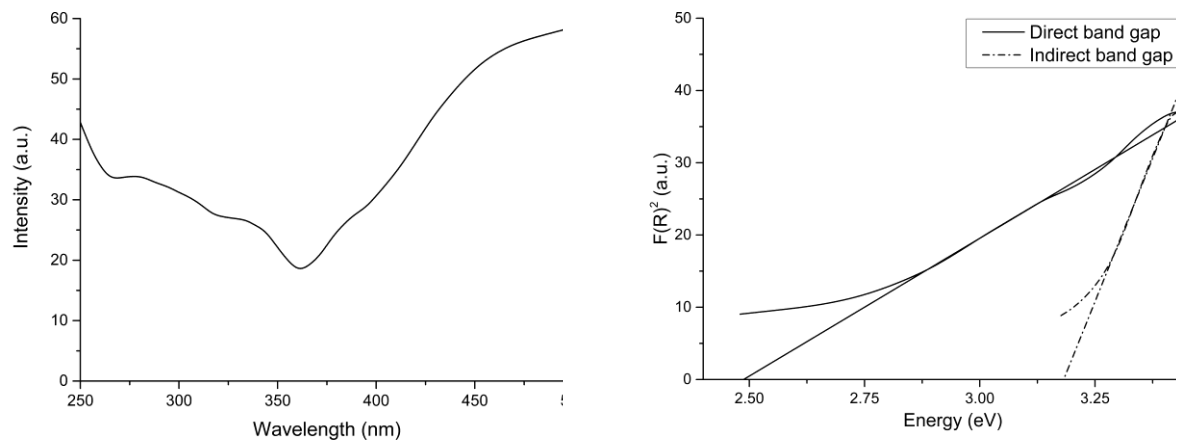


Figure 1. Diffuse reflectance spectrum and Kubelka-Munk function with direct and indirect band gap calculation

3.3. Luminescence properties

Figure 2 shows the luminescence spectrum of ceria nanoparticles suspension with an excitation energy of 5.00 eV. The spectrum has a maximum at region of 3.00 eV and a broad band in the long-wavelength region. The results of the PL spectrum decomposition indicate the presence of three overlapping elementary Gaussian bands with maximum 2.64 eV, 3.14 eV, 3.59 eV.

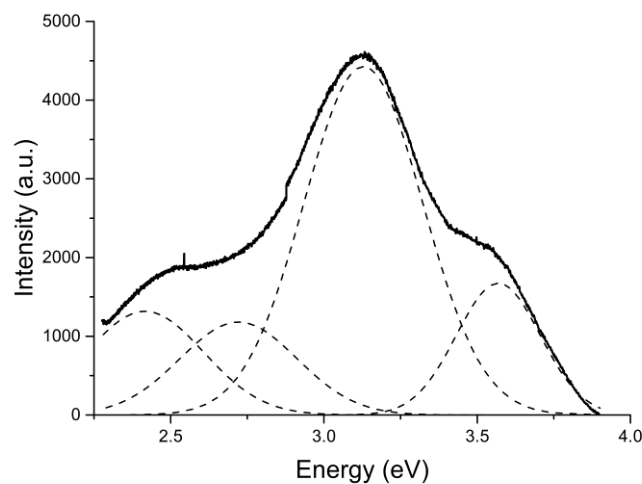


Figure 2. Luminescence spectrum ceria nanoparticles suspension (an excitation energy 5 eV) a Gaussian deconvolution

The peaks with energy 3.14 and 3.59 eV are characteristics for radiative transition in the Ce^{3+} ions. The $5d \rightarrow 4f$ radiative transitions in the luminescence spectra of Ce^{3+} ions are known to appear usually as a doublet of broad, partially overlapping bands [13]. These emission bands are caused by radiative transitions from the relaxed lower $5d$ -excited state to the ground $4f$ state split by the spin-orbit interaction into two levels $^2F_{5/2}$ and $^5F_{7/2}$.

The weak band observed in the PL spectrum in the region of 2.64 eV could be associated with the emission of F^0 centers related to the formation of oxygen vacancies.

Recently, nanoparticles have been shown to have similar properties and have high catalytic activity and have been used as fuel additives or biological agents. Thus, we can assume that these nanoparticles will be widely used in various fields of science and industry.

4. Conclusion

In the present work a high defective ceria nanoparticles obtained by the method of electron beam evaporation in a low-pressure gas atmosphere was studied. We found luminescent active centers, probably associated with the presence of Ce^{3+} ions and oxygen vacancies. The values of E for direct and indirect transitions were determined.

It can be concluded that by using an electron beam evaporation method actually synthesized nanoparticles of cerium dioxide, characterized by a high degree of defects, which causes the observed luminescence and optical properties.

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